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EXPERIMENTAL BASIS FOR MAXIMUM PERMISSIBLE CONCENTRATIONS OF CERTAIN SHALE PHENOLS IN THE WATER OF RESERVOIRS

[Eksperimental'noye obosnovaniye predel'no dopustimykh kontsentratsiy nekotorykh slantsevykh fenolov v vode vodoyemov]

by

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Waste waters which contain phenol are formed during thermal treatment of solid fuel: bituminous and lignite coals, wood, peat and shale oils. In the waste waters of enterprises during processing of this fuel there are various monatomic and diatomic phenols which are a very valuable industrial product and after their recovery from the waste waters find wide use in the national economy of the country.

However, part of the phenols, in spite of the measures taken for utilizing them in industry and in existing purifying equipment systems, remain in the discharge and get into surface reservoirs widely used for the water supply of the population. In this connection, the problem of hygienic standardization arises, that is, a scientific basis for the

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maximum permissible concentrations of harmful substances in water since in most cases to completely eliminate all contaminants from waste water is not possible.

The above mentioned was the goal of a number of scientists in the field of protecting reservoirs directed at an experimental base for the maximum permissible concentrations (PDK [predel'no dopustimyye kontsentratsiya, maximum permissible concentrations]) of phenols in the water of reservoirs coming from waste water of enterprises for processing fuel shales.

The basic direction for modern hygienic science and, in particular, public health, requires studying the effect of factors of an environment with low intensity on the sanitary conditions of life and the health of the population [9]. Because of this, for a basis for hygienic standards of the content of phenol substances getting into reservoirs from waste water, we made a detailed study of the properties of each of them. Then, the problem arose not only of clarifying the character of degree of contamination of the phenol substances but also determining the level of safety as it is adopted in research on hygienic standardization in sanitary protection of reservoirs [10].

A study of specific phenol substances of shale waste waters, as a rule, we began with an evaluation of their organoleptic properties, effect on odor, taste and coloration of the water. The subsequent stage of the experimental research on hygienic standards included an evaluation of the effect of the substances mentioned on the sanitary regimen of reservoirs, which can be judged according to the condition of their processes of natural self-purification from organic contaminants.

In view of the absence of adequate data on the toxic dynamics of the substances being studied, research on experimental animals was begun with a rigid test for establishing the average-lethal dose by a method of test analysis [7] and for the first criterion in the evaluation of toxicity of the substances being studied. For the purpose of a more complete general characterization of toxicity visible sensitivity and cumulative properties, in certain cases sub-rigid tests were made for determining the peculiarities of toxic dynamics.

For the medical and toxological characteristics of phenols, a chronic experiment was made. A good deal of attention was given to the effect of phenols on the central nervous system by studying the conditioned reflex activity of test animals. Moreover, methods were used which permitted clarifying the changes in protein and carbohydrate metabolism, and phenols were determined in the urine. On conclusion of the experiment, an evaluation was made of changes of pathomorphological character of internal organs and the content of vitamin C and sulfhydryl groups in homogenates of internal organs. The results obtained from experiments were treated with methods of variation statistics [1, 3].

The phenols of waste waters of shale oil industries are a mixture consisting of 85-90% diatomic and 10-15% monatomic phenols [5].

Monatomic phenols are a dark-brown viscous liquid with sharp odor, which dissolves well in water. The boiling temperature of this fraction of phenols is in a range from 180 to 270° C.

The odor of monatomic phenols is characterized as "unpleasant," "phenol"; the taste (with low concentrations)--as "sweetish," when large--as "bitter" and "phenol." The threshold of odor and taste for

monatomic phenols is set at a level of 0.05 mg/ℓ, odor during chlorination--0.025 mg/ℓ.

In the sanitary procedure of an experimental reservoir, monatomic phenols in concentrations up to 0.5 mg/ℓ did not show an effect and at 1.0 mg/ℓ cause a certain slowing down of processes of biochemical demands for oxygen.

In the chronic medical-toxological experiment on white rats and rabbits it was established that only the largest of the test doses (1/10 LD_{50} or 38.6 mg/kg) caused, during a 7-month peroral introduction, certain changes in the functional condition of the organism reflected in a proved increase in blood pressure, tendency to lose body weight and in histological changes in the form of parenchymatous dystrophy. This dose must be considered effective. When introducing 1/100 and 1/1000 LD_{50} such changes were not observed.

Diatomic phenols are a resin-type dark-brown substance, which dissolves slowly in cold water; boiling temperature of this mixture is 271--315° C.

The limiting indication of harmfulness of diatomic phenols is organoleptic (coloration) which is set at a level of 0.14 mg/ℓ for reservoirs of first type of water use and 0.26 mg/ℓ for the sea. The threshold concentration for the effect of diatomic phenols in sanitary procedure of reservoirs is 0.5 mg/ℓ

An evaluation of the functional state of the organism of test animals during lengthy peroral intake of diatomic phenols showed that the highest dose of those given--1/10 LD_{50} (63.3 mg/kg)--is threshold, and 1/100 LD_{50}--ineffective. The latter dose was almost 1000 times

higher than threshold according to the limiting organoleptic indication of harmfulness of diatomic phenols. Both the monatomic and diatomic phenols showed relatively low toxicity. Here, the common limiting factors characteristic were: variation in blood pressure and histological changes of internal organs in the form of dystrophy.

Moreover, monatomic and diatomic phenols to the same degree are characterized by a capacity to slow down biochemical processes in the reservoirs beginning with the same level of concentrations. The limiting characteristic of harmfulness is also common for them--organoleptic. However, with all the significant similarity of the group characteristics of monatomic and diatomic phenols, an essential difference was observed between them. This involved the fact that with the same limiting organoleptic characteristic of harmfulness, a difference in the character of this characteristic was observed: monatomic phenols are capable of inducing chlorophenol odors with smaller concentrations in water, diatomic--to change the coloration of the water.

However, one should note that the group characteristics mentioned of phenols are given on the basis of dividing phenols according to distillation of these groups according to their peculiarities by physical characteristic--difference in boiling temperature. Thus, one should not state that all individual phenols which can be called monatomic or diatomic phenols by chemical composition will completely correspond to the group characteristics indicated by us. This requires further research in order to give more completely detailed characteristics of individual examples.

According to the data of Yu. E. Lillye and Kh. A. Kundel' [4], diatomic phenols of wate water are a mixture of various alkyl producing resorcins among which 5-methyl resorcin is predominant. The monatomic part of the shale oil phenols consists of hydroxybenzene, cresols, dimethylphenols and higher phenols among which α- and β-naphthol were identified. In this mixture, a significant part is isomers of dimethylphenol (DMF [dimetilfenol, dimethylphenol] therefore, we carried out work on their hygienic standardization.

An evaluation of the functional state of the organism of white rats when given isomers of DMF was done on the basis of factors of change displacements in red and white blood cells, prothrombin time, blood pressure without and under the effect of adrenalin, the contents of total protein and protein fractions, and also--the SH-groups of blood serum, the quantity of free and bonded phenols given off in the urine, antitoxin functions of the liver, capacity to summarize subliminal impulses; conditioned-reflex activity and posthumously, the content of the SH-groups and vitamin C in homogenates of the liver, kidneys and spleen.

It was shown that the DMF isomers studied only during innoculation with doses 1/5 LD_{50} (6/mg/kg 2,6-DMF and 14 mg/kg 3,4-DMF) caused loss in body weight, a decrease in the content of hemoglobin in the blood, a breakdown in processes of normalization of blood pressure after introducing adrenalin, an increase in content of sulfhydryl groups and tissue of the liver, spleen and brain. In the histological structure of the liver, kidneys and muscles of the heart, parenchymatous dystrophy was observed.

Doses of 0.6 mg/kg 2,6-DMF (12 mg/l) and 1.4 mg/kg 3,4-DMF (28 mg/l) did not cause pathological shifts in the organism and changes in the pathomorphological picture of internal organs.

Threshold concentration, according to the effect of DMF isomers, on the sanitary procedure of reservoirs were established for 2,5- and 2,6-DMF at a level of 2.5 mg/l and for 3,4- and 3,5-DMF--0.5 mg/l.

It is clear that the limiting characteristic of harmfulness for all DMF isomers is organoleptic (odor). The threshold for this factor for 2,6- and 2,5-DMF is 0.12 mg/l and for 3,4- and 3,5-DMF--0.25 mg/l. The concentrations indicated were recommended as hygienic standards.

Among various alkyl-producing resorcins, in the composition of shale oil diatomic phenols, 5-methylresorcin-orcinol (5-MR [methylrecorcin-orcin]), are individual methyl-producing resorcin, given off from the shale oil waste waters in pure form.

Experiments in studying the effect of 5-MR on organoleptic properties of water tells us that the most significant factor is its effect on coloration of the water. The threshold concentration, according to this factor, is at a level of 1 mg/l (for reservoirs of the first class of water use) and 5 mg/l for sea water.

With concentrations of 5-MR mg/l there begins an increase in requirements for oxygen and retarding processes of nitrification in the reservoir. An evaluation of the functional state of the organism with inoculation of the animals with 5-MR is done on the basis of the factors of the degree of effect of it on the composition of white and red blood cells, blood pressure with and without adrenalin load, content of total protein and protein fraction and sulfhydryl groups of blood serum, on

the summarized-threshold factor and conditioned reflex activity of white rats.

Research indicated that only with innoculation with a dose of 1/25 LD_{50} (33.8 mg/kg) does one observe certain weakening of the inhibiting process: a slowing down of fading of the positive conditioned reflex and a delay in the phenomenon and strengthening of differentiated reactions to the buzzer, a decrease in the total-threshold factor, a change in the leukocyte formula of the blood (an increase in the number of eosinophils), an increase in the quantity of free and bonded phenols given off in the urine, a decrease in the content of vitamin C in the adrenal glands, and also changes in the pathomorphological picture expressed in protein and fat dystrophy of the structure of the liver and kidneys.

The introduction of a dose of 8.4 mg/kg (1/100 LD_{50}) causes only a certain weakening in the inhibiting processes in conditioned reflex activity of white rats expressed in slowing down of the fading of the positive conditioned reflex, therefore, this dose is evaluated as ineffective.

During compilation of the data of experimental research, it became clear that the limiting factor of harmfulness of 5-MR is its effect on the organoleptic properties of the water, and the threshold concentration according to this characteristic of harmfulness can be recommended at a level of 1.0 mg/l. This concentration is approximately 170 times lower than the ineffective concentration for the sanitary and toxological characteristic of harmfulness The maximum permissible concentration for 5-MR is proposed as 1.0 mg/l according to the organoleptic characteristic

for harmfulness (coloration).

The experimental research done and certain bibliographical data permit establishing a generalized form of factors which characterize the sanitary safety of phenol substances of waste water from shale oil processing industries (Table 1). The phenols shown in the Table even in insignificant concentrations are dangerous to the health of the population or make conditions for water utilization worse.

From the waste waters of shale oil combines not just a single substance flows into the reservoirs but often at the same time several of the substances studied by us. Therefore, we did thorough research on establishing the degree of negative effect of phenols when they are combined in water. For this purpose, studies were made with monoatomic phenols, whose limiting factors of harmfulness is organoleptic (hydroxybenzene, isomers of DMF, m-cresol and a-napthol) and sanitary-toxicological) m-cresol and ß-napthal).

S.N. Cherkinskiy developed theoretical bases for standardizing conditions for simultaneous contamination of water reservoirs with certain harmful substances [11]. He determined the principle of summarizing the effect and necessity for decreasing the quantity of maximum permissible concentrations of harmful substances with uniform limiting factor of harmfulness by several times inasmuch as the harmfulness substances were combined.

This important position led to water-sanitary legislation; however, in view of the possible danger of the potency of harmful effect of various ingredients of industrial contaminants, limited according to the sanitary-toxicological factor of harmfulness, it is necessary to

TABLE No 1 BASIC HYGIENIC PARAMETERS FOR PHENOLS OF WASTE WATERS OF SHALE OIL PROCESSING INDUSTRIES

Phenol	Factors of Harmfulness						Annotation
	Organoleptic Threshold, mg/ℓ			Total-sanitary (Threshold) Mg/ℓ	Sanitary-toxicological (Ineffective)		
	Odor	Taste	Coloration		mg/kg	mg/ℓ	
1. Mixture of monatomic phenols	0.025[1] 0.05	0.05	--	0.5	3.86	77.2	
2. Hydroxylbenzene	0.001[1] 1.0	0.001[1] 1.0	--	--	0.5	10	Data of A.I. Kostovetskiy (2)
3. m-cresol	0.2	0.002 0.001[1]	--	0.1	0.005	0.1	Data of M.N. Pavlenko and V.A. Kuznetsova
4. n-cresol	0.1	0.05 0.002[1]	--	0.1	0.0001	0.002	(6)
5. 2,5-DMF	0.25 0.12[2]	0.25	--	2.5	--		
6. 2,6-DMF	0.25 0.12[2]	0.12	--	2.5	0.6	12	
7. 3,4-DMF	5.0 0.25[1]	5.0	--	0.5	1.4	28	
8. 3,5-DMF	5.0 0.25[1]	5.0	--	0.5	--		
9. α-naphthol	0.1	0.25	0.4	0.4	0.05[1]	1.0	Data of Yu. A. Rakhmanin (8)
10. β-naphthol	0.8	0.75	0.4	0.4	0.02[3]	0.4	
11. Mixture of diatomic phenols	0.25	0.22	0.14	0.5	6.33	126.6	
12. Resorcin	40	1.0	--	0.1	0.5	10	Data of A.I. Kostovetskiy (2)
13. 5-MR	2300	900	1.0	0.1	8.4	168	

[1]During chlorination
[2]During heating
[3]In the list for the most sensitive animals (female cats) to the effect of α- and β-naphthols.

test their combined effect experimentally. This research is expedient for substances with organoleptic and general sanitary factors of harmfulness, although the principle of summarizing has not yet been accepted as a basic concept.

The study in test conditions of the combined effect of 7 monatomic phenols (hydroxy benzene, m-cresol, 2,5-, 2,6-, 3,4- and 3,5-DMF and α-naphthal) limited according to organoleptic factors of harmfulness, permitted establishing that they actually must be standardized according to the principle of total effect.

In a similar plan, a study was made of the combined effect of π-cresol and β-naphthol which are limited according to sanitary-toxological factor of harmfulness. With the intake by animals during an 8 month period of doses of substances being studied at a level of their maximum permissible concentrations, there were only very slightly expressed functional changes in conditioned reflex activity due to weakening of the inhibiting process, a decrease in total-threshold factor (in the second half of the test), a decrease in the quantity of lymphocytes in the peripheral blood, and certain breakdown in the process of normalization of blood pressure under adrenalin load. In doses corresponding to half the PDK, π-cresol and β-naphthal did not show any kind of damage.

Thus, the studies made supported the important theoretical position in the field of hygienic standardization on summarizing the harmful effect of substances with sanitary-toxological limiting factors of harmfulness.

When observing these conditions, the reliability of using hygienic

standards increases and are guaranteed acceptable in medical relation to conditions of water use in regions located below enterprises which are thermally processing shale oils.

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